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Electrochemical synthesis and electrochromic application of a novel polymer based on carbazole

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ABSTRACT

The compound containing carbazole and thiophene, named as B1 was synthesized with 4-(9H-carbazol-9-yl) phenol and 3,4-dibromo thiophene. Additionally, the electrochemical polymer of B1 was synthesized and coated onto an ITO-glass surface via electrochemical oxidative polymerization. The electrochemical synthesis of the polymer was performed both in 0.05 M LiClO₄ supporting electrolyte in AN/BF₃EtE (1:1, v/v) and an AN/LiClO₄ solvent/electrolyte solution. The compounds were characterized by FT-IR and NMR techniques. The spectroelectrochemical and electrochromic properties of this polymer was measured as the percent transmittance (%T) at its point of maximum contrast. According to the electrochromic measurements, the synthesized polymer had a blue color when it was oxidized, and also when it was reduced, it had a transparent color. Additionally, redox stability measurements indicates that the polymer had a high stability and it could be used to produce new polymeric electrochromic devices and also, it was a good candidate for electrochromic devices (ECDs) applications.

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1. Introduction

Electrochromic materials have the reversible color change of an electro-active material through an electrochemical oxidative reaction [1–3]. These materials, which are able to exhibit color and transmissivity changes upon an electrical effect, and they are envisaged to be applied in a wide range of applications such as smart windows, electronic displays, LED devices and camouflage textiles [4–6]. Electrochromic materials that are prepared through an electrochemical polymerization technique form an insoluble polymer film directly on the ITO substrate. Processable polymeric EC materials [7–15] are thus highly sought after to lower the production cost and hence to render more competitiveness for the commercialization of these materials.

Many semi-conducting polymeric materials have recently been synthesized via electropolymerization [16]. Some of these synthesis methods, including copolymerization with the bonding of certain functional groups [17–21] modified with electro-active moieties such as, thiophene [22], fluorine [23], carbazole and pyrrole, which have been used to form electrochromic polymers with useful properties for their various applications [24–25].

Recently electrochromic applications have been developed rapidly, and also more electrochromic polymers are needed. The color scale is a very important for electrochromic applications. Therefore, there is a need to the synthesis of new polymers.

Herein in this study, we primarily aimed to investigate whether the electrochromic properties of the synthesized monomer (B1). Additionally, we reported the electrochemical synthesis of a new polymer containing carbazole and thiophene units. For this purpose, the compound named as B1 was first synthesized via HBr elimination [26,27]. Then, the named polymer as poly-bis-4-(9*H*-carbazol-9-yl) phenyl-3,4-diyloxy thiophene P(B1) was synthesized via electrochemical polymerization both in 0.05 M LiClO₄ supporting electrolyte in AN/BF₃EtE (1:1, v/v) and an AN/LiClO₄ solvent/electrolyte solution. UV–vis, FT-IR, ¹H–NMR and CV were used for structural characterization. According to the obtained data, the synthesized polymer could be used in electrochromic devices applications.

2. Experimental

2.1. Materials

Carbazole, potassium carbonate (K_2CO_3), potassium hydroxide (KOH), 18-Crown-6, ethanol, methanol, chloroform (CHCl₃), acetonitrile (AN), tetrahydrofuran (THF), 3,4-dibromo thiophene and toluene were supplied from Merck Chemical Co. (Germany) and used as received. 4-iodo phenol was supplied from Aldrich





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Chemical Co. (USA). 18-Crown-6 was used as phase transfer catalysis. Boron trifluoride ethyl etherate (BF_3EtE) was supplied from Fluka Chemical Co.

2.2. Synthesis of 4-(9H-carbazol-9-yl) phenol (A1)

Firstly, carbazole (1.672 g, 0.01 mol), KOH (0.842 g, 0.015 mol), 18-Crown-6 (0.01 g, 0.04 mmol) as phase transfer catalysis were dissolved in toluene (20 mL) and this reaction mixture was vigorously stirred at 110 °C under argon for 1 h. A solution of 4-iodo phenol (3.3 g, 0.015 mol) in toluene (10 mL) was slowly added to this reaction mixture, and it was refluxed at 110 °C under argon and stirred for 16 h (Scheme 1). The reaction mixture was then cooled to room temperature. Then, the reaction mixture poured into the 150 ml of ethanol and stripped off by a rotary evaporator. The product was recrystallized from methanol and dried in a vacuum desiccator [28]. (Yield: 60%).

A1: *FT-IR* (*cm*⁻¹): v (O–H, phenolic) 3170 m, v (C=C phenyl) 1560, 1475 s, v (C–N) 1450 s, v (C–O) 1236 s. ¹*H* NMR (DMSO): δ_H ppm, 7.512, 7.492 (d, 2H, Ha), 7.411, 7.391, 7.374 (t, 2H, Hb), 7.183, 7.164, 7.144 (t, 2H, Hc), 7.271, 7.249 (d, 2H, Hd), 8.129, 8.110 (d, 4H, He, Hf), 11.486 (s, 1H, –OH). Calculated: C, 83.40; H, 5.02; N, 5.41. Found: C, 84.70; H, 4.85; N, 5.39.

2.3. Synthesis of B1 via HBr elimination

The synthesis reaction of bis-4-(9H-carbazol-9-yl) phenyl-3,4-diyloxy thiophene (B1) had a two-stage process. In the first stage, K_2CO_3 (0.552 g, 0.004 mol) and A1 (0.518 g, 0.002 mol) were dissolved in THF (20 ml) and stirred for 1 h. In the second stage, 3,4-dibromo thiophene (0.242 g, 0.001 mol) was added to this reaction mixture. The reaction mixture was stirred with a magnetic stirring bar for 16 h under argon atmosphere. This reaction solution was poured into 200 ml of water and the precipitated crude product was collected and filtered. The obtained compound was dried in a vacuum oven at 60 °C [29] (Yield \sim 50%). B1 was obtained as a light yellow colored powder. Additionally, the chemical structure of the compound was shown in Scheme 2.

B1: *FT-IR* (*cm*⁻¹): *v* (C=C phenyl) 1627, 1598, 1490 s, *v* (C–N) 1450 s, *v* (C–O–C) 1238, *v* (C–S) 746, 725 s. ¹*H* NMR (*DMSO*): δ_H *ppm*, 7.518, 7.497 (d, 4H, Ha, Hd), 7.419, 7.399, 7.381 (t, 2H, Hb), 7.189, 7.170, 7.150 (t, 2H, Hc), 8.133, 8.114 (d, 4H, He, Hf), 7.885 (s, 1H, Hg). *Calculated:* C, 80.17; H, 4.34; N, 4.68. S, 5.34. *Found:* C, 79.84; H, 5.24; N, 5.01; S, 5.30.

2.4. Electrochemical polymerization

Cyclic voltammetry (CV) measurements were performed using an Ivium potentiostat at different potential scan rates. CV was employed to assay the electrical activity of the compounds and determine their oxidation–reduction peak potentials. The system consists of a CV cell containing an indium tin oxide (ITO)-coated glass plate as the working electrode, platinum wire as the counter electrode and Ag wire as the reference electrode. The CV measurements were separately performed using both a (0.05 M)



Scheme 1. Synthesis of 4-(9H-carbazol-9-yl) phenol (A1).

LiClO₄/acetonitrile (AN:BF₃EtE) (1:1, v/v) and LiClO₄/acetonitrile (AN) without BF₃EtE solvent mixture at room temperature during 200 s [30]. The electropolymerization reactions involved dissolving B1 (0.1 M) in 10 ml of supporting electrolyte in AN, and placing the resulting solution into the CV cell. Next, the solution was repeatedly scanned between -0.1 and 1.2 V. The resulting polymer films were washed with AN to remove LiClO₄ and BF₃EtE [31] (Scheme 3).

2.5. Structural characterization

The FT-IR spectra of the compounds were recorded on a Perkin Elmer RX I FT-IR spectrometer with KBr pellets in the range 4000–400 cm⁻¹. ¹H NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz) were also recorded using DMSO-d₆ as the solvent at 25 °C. Tetramethylsilane was used as an internal standard. An Ivium potentiostat was used to supply a constant potential during the electrochemical syntheses and cyclic voltammetry experiments. An Agilent 8453 UV-vis spectrophotometer was used for the spectroelectrochemical studies and characterization of the compounds.

2.6. Spectroelectrochemical characterization

The polymer films, which had been electrochemically deposited onto ITO-coated glass slides, were used to perform the spectroelectrochemical experiments. Spectroelectrochemical and electrochromic measurements were conducted in a LiClO₄/AN solution using an Ag wire as the reference and a Pt wire as the auxiliary electrode. The data obtained from the cyclic voltammetry measurements were used for the spectroelectrochemical measurements of the polymer film [32]. These measurements were performed to account for the absorption spectra of the polymer film under the applied potentials. The spectroelectrochemical cell included a quartz cuvette, an Ag wire (RE), a Pt wire counter electrode (CE) and the polymer film on ITO/glass as a transparent working electrode (WE). These measurements were performed in a 0.05 M LiClO₄ supporting electrolyte in both AN/BF₃EtE and only LiClO₄/AN without BF₃EtE. Cycle number was chosen as 5 for each CV measurements [33].

3. Results and discussion

3.1. NMR spectra and FT-IR spectra

Synthesized compounds have different colors like light yellow and violet. While A1 has a violet color, B1 has a light yellow. Additionally, when A1 is a crystalline structured, B1 is a powder form.

The FT-IR spectra of the synthesized compounds are recorded. 4-(9*H*-carbazol-9-yl) phenol (A1), which possesses a phenolic —OH stretching peak, C—N and C—O peaks at 3170, 1450 and 1236 cm⁻¹, respectively [34]. The FT-IR spectrum from A1 shows that the —NH peak belong to carbazole unit disappears after the reaction [35]. This indicates that the reaction takes place and that the target product form. The results of these FT-IR studies clearly indicate that polymerization is successfully achieved.

The FT-IR spectrum from B1 shows the following absorption peaks: 1627, 1598 and 1490 cm⁻¹ (from the aromatic C=C stretching), 1238 cm⁻¹ (from the C–O stretching), 1450 cm⁻¹ (from the C–N stretching) and 746, 725 cm⁻¹ (from the C–S stretching) [20,34]. Due to thiophene groups in the structure of B1, the peak related to C–S bonding is observed at 746 and 725 cm⁻¹, as expected [36]. Moreover, the presence of these peaks confirms that the reaction successfully occurs.



Scheme 2. Synthesis of bis-4-(9H-carbazol-9-yl) phenyl-3,4-diyloxy thiophene (B1).



Scheme 3. Electrochemical synthesis of poly-bis-4-(9H-carbazol-9-yl) phenyl-3,4-diyloxy thiophene P(B1).

The FT-IR spectrum of poly-bis-4-(9*H*-carbazol-9-yl) phenyl-3,4-diyloxy thiophene P(B1), which is synthesized via electrochemical polymerization, is shown in Fig. 1. As seen in Fig. 1, it can be said that the peak at 3207 cm^{-1} comes from humidity in the polymer. The peak at 1600 cm^{-1} is related to -NH (-CH=N-) group in the carbazole units [32,33,35]. The peaks at 1543 and 1447 cm^{-1} are attributed to the aromatic C=C stretching in the carbazole, the phenolic benzene and thiophene groups. The C-C stretching peak is observed as a widespread and sharp peak at 1038 cm^{-1} , as expected. This peak clearly confirms that the electropolymerization reaction successfully occurs. Also, it can be said that the polymer is successfully obtained.

According to ¹H NMR spectrum of A1, the characteristic peak related to phenolic —OH group is obtained at 11.486 ppm, as expected [37]. The protons related to carbazole units are observed in the range of 7.512 and 7.144 ppm. Briefly, the ¹H NMR spectrum of A1 shows resonance signals for protons from the phenolic —OH, carbazole group and benzene rings [38]. The characteristic signals at 8.129, 8.110, 7.512, 7.492, 7.271, 7.49, 7.411, 7.391, 7.374, 7.183, 7.164 and 7.144 ppm are attributed to the carbazole moiety and benzene rings in the structure of A1. It indicates the reaction had gone to completion. Additionally, the peak at 11.486 ppm is related to the phenolic —OH group, which is observed as a splayed peak. The named as Hb and Hc in the structure of A1 are obtained as a triple peak, as expected. This result completely explains the monomer structure (A1).

For B1, a new peak signal is observed in its spectrum due to add to 4-(9*H*-carbazol-9-yl) phenol of thiophene group and this signal is attributed to thiophene group. In its spectrum the named proton as Hg is observed as a single peak at 7.885 ppm, as expected [35]. This confirms that it is added to the structure of thiophene. Additionally, as seen in its FT-IR spectrum it can be clearly seen that C—O—C bonding forms at about 1238 cm⁻¹ (Fig. 2).

3.2. Cyclic voltammetry

Thiophene derivatives readily undergo a one-electron oxidation to form a radical cation (polaron) when their α -positions are

unsubstituted. Kava and his friends explained the mechanism of electrochemical polymerization progressing on thiophene units [39]. Continual oxidation affords higher ordered oligomers via a radical coupling mechanism that ultimately forms a polymer [40]. In literature, electrochemical reaction mechanism is described in detail by Darmanin and Guittard [41]. As known, electro-active groups as carbazole, pyrrole, thiophene are expected to be firstly oxidized species and the polymerization starts by forming the polaron structure (radical cation) of carbazole, which obtains by applying the potential. Thus, the monomer oxidizes to form its radical cation. The other monomers (carbazole, thiophene, pyrrole etc.) are added to these radical cations (called polarons). After reduction process, the polymer chain is extended by adding the monomer units. The studies related with the electropolymerization progressing on carbazole units are available in literature. According to literature, it can be said that the electrochemical polymerization progresses on carbazole units up to 1.3 voltage [42.43].

The cyclic voltammogram of P(B1) in an AN/LiClO₄ solvent/electrolyte solution namely the absence of BF3EtE possesses one consecutive oxidation peak at 0.95 V and one reduction peak at about 0.75 V when it is scanned from +0.3 to +1.4 V. As seen in Fig. 3a, the increasing oxidation peak potential at 0.95 V after repeated scans for P(B1) is evidence of the electropolymerization, the formation of a poly-conjugated structure and a reduction in the electrochemical band gap. The decreasing in the peak current after repeated scans occurs because of polymer adsorption onto the electrode surface, which causes a sensitivity decrease in the electrode. The decreased oxidation potential after repeated scans is evidence of electropolymerization. The CV behavior of P(B1) shows an increase in peak intensity for the repeated scans [44]. When the polymer is oxidized, it has a blue color between +1.0 and +1.4 V, and also it has a light yellowish between +0.5 and +0.9 V. Additionally, when the film is reduced, it has a transparent color in the range of +0.3 and +0.5 V. To investigate the CV behavior of the polymer P(B1), we performed CV studies in the presence of BF₃EtE using the same experimental conditions as above (see Fig. 3b). The measurements were performed in a 0.05 M LiClO₄



Fig. 1. The FT-IR spectrum of poly-bis-4-(9H-carbazol-9-yl) phenyl-3,4-diyloxy thiophene P(B1).



Fig. 2. ¹HMR spectrum of bis-4-(9H-carbazol-9-yl) phenyl-3,4-diyloxy thiophene (B1).

supporting electrolyte in AN/BF₃EtE (1:1, v/v) between -0.2 and +1.2 V potentials. The voltammograms changed drastically. There was an incremental decrease at reduction potential and the oxidation potential of P(B1) differed from those of previous voltammogram. This means that the oxidation peak potential shifts to 0.7 from 0.95 V, and also the reduction peak potential shifts to about 0.4 V from 0.75 V when it is scanned between -0.2 and +1.2 V. After each scanning, an increase in the oxidation peak confirms that the electrochemical polymerization reaction occurs. Additionally, it can be clearly said that the polymer film is obtained under these conditions, namely in the presence of BF₃EtE. When

the polymer film is oxidized, a green color is obtained between +0.8 and +1.2 V, and also it has a yellowish green between +0.5 and +0.8 V. In addition, when the polymer film is reduced, it has a transparent color in the range of -0.2 and +0.5 V. During the growth of the P(B1) film, as cycle number increases reduction coupling shifts at a lower potential, which can be attributed to the oxidative doping (i.e., polaron and bipolaron formation) and reductive dedoping of the formed polymer [45]. Cyclic voltammograms of P(B1) are shown in Fig. 3a and b, respectively. Fig 3c shows CV voltammogram of P(B1) between -0.1 and +1.2 V after 200 s. As seen in Fig. 3c, the polymer film is quite stable.



Fig. 3. Cyclic voltammograms for repeated scans of P(B1) in an (a) AN/LiClO₄ solvent/electrolyte solution, (b) and (c) 0.05 M LiClO₄ supporting electrolyte in AN/BF₃EtE (1:1, v/v) (scan rate: 0.4 V/s, cycle numbers: 5).

3.3. Scan rate dependence of the peak currents

Scan rate measurements were performed in a solution 0.05 M LiClO₄/AN:BF₃EtE containing 0.1 M the monomer B1 at constant potential of 1.2 V during 200 s. Scan rates were adjusted as 400, 300, 200, 100, 50, 20 mV/s, respectively (see Fig. 4a). In scan rate study, the peak current changes were examined depending on scan rate. The obtained graph by plotted depending on scan rate of the oxidation and reduction peak potentials signs a linear increase. Also, it shows that the electropolymerization is not controlled diffusion and the polymer film is storaged very well onto ITO surface. The current responses are directly proportional to the scan rate indicating that the polymer film is electro-active and well adhered to the electrode. The scan rates for the anodic and cathodic peak currents show a linear dependence as a function of the scan rate as illustrated in Fig. 4b. This demonstrates that the electrochemical processes are not diffusion limited and reversible even at very high scan rates [46].

3.4. Spectroelectrochemical properties

Spectroelectrochemistry is a good method for examining changes in the optical properties of a polymer on ITO upon applying a potential. It also provides information about the properties of the conjugated polymer, such as the band gap (E_g) and intergap states that appear upon doping. The polymer film was coated onto ITO at a constant potential of +1.2 V during 200 s. After the polymer film was washed with AN to remove LiClO₄ and BF₃EtE, its spectroelectrochemical measurements were performed at different potentials with 0.1 M B1 monomer concentration in 0.05 M AN/LiClO₄ and LiClO₄/AN:BF₃EtE (1:1, v/v) electrolyte solutions namely for two different solvent/electrolyte systems. Fig. 5a shows the changes in the absorption spectrum of P(B1) in an AN/LiClO₄ solution under various applied potentials. As the polymer devices oxidized, the intensities of their π - π ^{*} transitions decreased, and their charge carrier bands at approximately 800-900 nm increased because of polaron formation [39]. However, in this study any $\pi - \pi^*$



Fig. 4. (a) Exchange graph of the peak currents depending on scan rate and (b) graph of a linear dependence as a function of the scan rate.



Fig. 5. Spectrochemistry and color changes of the polymers in (a) 0.05 M AN/LiClO₄ solvent/electrolyte solution, (b) LiClO₄ supporting electrolyte in AN/BF₃EtE (1:1, v/v).

transitions could not be observed in 0.05 M AN/LiClO₄ electrolyte solution system. Therefore, spectroelectrochemical measurements were conducted in a LiClO₄/AN:BF₃EtE (1:1, v/v) electrolyte system. The π - π ^{*} transitions related to P(B1) was observed at 320 nm, and also polaron and bipolaron band formations at 400 nm and 670 nm, respectively. As emphasized, the band gap (E_{σ}) was calculated as 3.24 eV for the polymer. The oxidized form of P(B1) possesses an absorption maximum at 400 nm, which corresponds to an light blue color. Increasing the degree of oxidation in P(B1) gradually increases the absorbance intensity at 670 nm, and simultaneously, shifts a bit this band to shorter wavelength (hypsochromic shift or shift to blue), which corresponds to the presence of positive carriers and the formation of fully doped polymeric chains. As the doping level increased, the sub-gap absorption grew at the expense of the $\pi - \pi^*$ transition [47]. The color changes of the synthesized polymer films both in 0.05 M LiClO₄ supporting electrolyte in AN/BF3EtE (1:1, v/v) and an AN/LiClO4 solvent/electrolyte systems at the various potentials are also shown as insert figure of Fig. 5. Fig. 5a is related to the color and absorbance changes of the polymer film in an AN/LiClO₄ solvent/electrolyte. Also, Fig. 5b is related to the color and absorbance changes of the polymer film in 0.05 M LiClO₄ supporting electrolyte in AN/BF3EtE (1:1, v/v).

3.5. Electrochromic performance and redox stability of P(B1)

The ability of a polymer to switch without delay and exhibit a sharp color change are very significant. Double potential step chronoamperometry was carried out to estimate the response time of the polymer film. The potential was stepped between fully oxidized and neutral states of the polymer film with a residence time of 5 s. During the experiment, the percent transmittance (%T) at the wavelength of maximum contrast was measured using a UV-vis spectrophotometer. The measurements were conducted using a single wavelength with obviously changing absorption intensity. The polymer film was deposited onto the ITO-coated glass slides under constant potential conditions, as mentioned above, and its absorbance was monitored at λ_{max} while switching between potentials. For P(B1) maximum contrast (%T) and switching time were

measured from Fig. 6 as 43% and 4 s for 670 nm by stepping the potential between 0.0 and +1.2 V with a residence time of 5 s. The stability of the redox states during the scans is the most property for an electro-active polymer to be useful in constructing new electrochromic devices [32,33,35,39,48]. Additionally, the ability of a material to exhibit a noteworthy color change is important for electrochromic applications. The synthesized electrochemical polymer on ITO-glass exhibits a transparent color in the reduced



Fig. 6. (a) Electrochromic switching of the optical absorbance of P(B1) at 670 nm in the presence of 0.1 M LiClO₄ in AN/ BF₃EtE (1:1, v/v) and (b) profiles of the device recorded during double step spectrochronoamperometry.



Fig. 7. Current–potential graph of P(B1) as a function of repeated scans at 400 mV/s: after 1st cycle plain, after 500 cycles dash.



Fig. 8. Absorbance changes of P(B1) depending on the applied various potentials for per 10 s.

states and a blue color in the oxidized states. The switching graph of P(B1) is given in Fig. 6.

Redox stability of the electro-active polymers towards multiple redox switching usually limits the utility as the electrochromic materials in electrochromic devices (ECDs) applications [46]. The main reasons for failure of electrochromic materials are high applied voltages and environmental conditions. To test the stability of the polymer, the potential was swept repeatedly between -1.0 and +1.2 V with a scan rate 400 mV/s. Between the first and 500th cycles there was a bit decrease in the current, and also this decrease or a loss of field was calculated as 4%. As a result, it can be said that the polymer has a high stability and it could be used in electrochromic devices (ECDs) applications (see Fig. 7).

The in situ polymerization kinetics related to the synthesized polymer was performed. According to this process, a constant potential of +1.2 V was applied to the polymer film by performing an absorbance measurement for per 10 s. These measurements were conducted for both 385 and 670 nm at two maximum absorbance wavelengths. Additionally, it can be said that the polymerization increases linearly up to 40 s in course of time and after 40 s, the polymerization increases linearly with the square root of the time. This is shown as insert figure of Fig. 8. This means that the polymerization is not controlled diffusion until 40 s and after 40 s the polymerization is controlled diffusion due to the formed double layer.

4. Conclusions

named polymer as poly-bis-4-(9H-carbazol-9-yl) The phenyl-3,4-diyloxy thiophene P(B1) was synthesized via electrochemical polymerization. This process was performed both in 0.05 M LiClO₄ supporting electrolyte in AN/BF₃EtE and an AN/LiClO₄ solvent/electrolyte solution namely the absence of BF₃EtE. The synthesized polymer had a blue color when it was oxidized, and when it was reduced it had a transparent color. Additionally, scan rate study dependence of the peak currents was conducted at a constant potential of +1.2 V during 200 s. The scan rates for the anodic and cathodic peak currents showed a linear dependence as a function of the scan rate. The spectroelectrochemical measurements of the polymer film were performed, and the maximum absorbance wavelengths were determined as 320 and 670 nm. Also, the optical band gap was calculated as 3.24 eV for the polymer film. The electrochromic performance of the synthesized polymer was determined, and also its maximum contrast (%*T*) and switching time were measured as 43% and 4 s at 670 nm by stepping the potential between 0.0 and +1.2 V with a residence time of 5 s. According to redox stability measurements, the polymer had a high stability and it could be used in electrochromic devices (ECDs) applications. Additionally, it can be said that the synthesized polymer could be a good candidate for the electrochromic display with relatively low potential (+1.2 V) due to the switching ability of this polymer.

References

- [1] R. Sydam, A. Ghosh, M. Deepa, Org. Electron. 17 (2015) 33.
- [2] G. Sönmez, H.B. Sönmez, C.K.F. Shen, R.W. Jost, Y. Rubin, F. Wudl, Macromolecules 38 (2005) 669.
- [3] A.A. Argun, P.H. Aubert, B.C. Thomson, I. Schwendeman, C.L. Gaupp, J. Hwang, N.J. Pinto, D.B. Tanner, A.G. MacDiarmit, J.R. Reynolds, Chem. Mater. 16 (2004) 4401.
- [4] V.K. Thakur, G. Ding, J. Ma, P.S. Lee, X. Lu, Adv. Mater. 24 (2012) 4071.
- [5] P.M. Beaujuge, J.R. Reynolds, Chem. Rev. 110 (2010) 268.
- [6] S. Mi, J. Wu, J. Liu, J. Zheng, C. Xu, Org. Electron. 23 (2015) 116.
- [7] A. Kerszulis, C.M. Amb, A.L. Dyer, J.R. Reynolds, Macromolecules 47 (2014) 5462.
- [8] W.T. Neo, C.M. Cho, J. Song, J.M. Chin, X. Wang, C. He, H.S.O. Chan, J. Xu, Eur. Polym. J. 49 (2013) 2446.
- [9] A.L. Dyer, E.J. Thompson, J.R. Reynolds, Appl. Mater. Interfaces 3 (2011) 1787.
- [10] S. Hellström, P. Henriksson, R. Kroon, E. Wang, M.R. Andersson, Org. Electron. 12 (2011) 1406.
- [11] C.M. Amb, A.L. Dyer, J.R. Reynolds, Chem. Mater. 23 (2010) 397.
- [12] J. Hwang, J. Ik Son, Y.B. Shim, Solar Energy Mater. Solar Cells 94 (2010) 1286.
- [13] H.J. Yen, G.S. Liou, Chem. Mater. 21 (2009) 4062.
- [14] C.G. Wu, M.I. Lu, S.J. Chang, C.S. Wei, Adv. Funct. Mater. 17 (2007) 1063.
- [15] M.E. Nicho, H. Hu, C. López-Mata, J. Escalante, Solar Energy Mater. Solar Cells
- 82 (2004) 105. [16] A. Adhikari, S. Radhakrishnan, R. Patil, I. Rahul, Synth. Met. 159 (2009) 1682.
- [17] W.O. Kenyon, G.P. Wough, J. Polym. Sci. 32 (1958) 83.
- [18] R.T. Swiger, J. Polym. Sci. 13 (1975) 1554.
- [19] J.A. Blanchette, J. Org. Chem. 23 (1958) 1117.
- [20] J.M.J. Frechet, M.J. Farrall, in: S.S. Labana (Ed.), Chemistry and Properties of Crosslinked Polymers, Academic Press, New York, 1977.
- [21] M.J. Farrall, J.M.J. Frechet, J. Org. Chem. 41 (1976) 3877.
- [22] I. Shen, K. Tsuchiya, K. Ogino, J. Polym. Sci. A: Polym. Chem. 46 (2008) 1003.
- [23] B. Ludwig, E.S. Tillman, Macromol. Chem. Phys. 206 (2005) 2143.
- [24] A. Lateulade, B. Grassl, C. Dagron-Lartigau, J. Francois, Polymer 47 (2006) 2280.
- [25] S. Chigwada, D.D. Jiang, C.A. Wikie, Thermochim. Acta 436 (2005) 113.

- [26] İ. Kaya, K. Temizkan, A. Aydın, J. Electroanal. Chem. 708 (2013) 54.
- [27] İ. Kaya, K. Temizkan, A. Aydın, Mater. Sci. Eng. B 178 (2013) 863.
- [28] L. Li, Y. Liu, H. Guo, Y. Wang, Y. Cao, A. Liang, H. Tan, H. Qi, M. Zhu, W. Zhu, Tetrahedron 66 (2010) 7411.
- [29] İ. Kaya, A. Aydın, Polym. Adv. Technol. 22 (2011) 951.
- [30] İ. Kaya, E. Bora, A. Aydın, Prog. Org. Coat. 77 (2014) 463.
- [31] İ. Kaya, A. Aydın, Prog. Org. Coat. 73 (2012) 239.
 [32] A. Aydın, İ. Kaya, J. Electroanal. Chem. 691 (2013) 1.
- [33] A. Aydın, İ. Kaya, Electrochim. Acta 65 (2012) 104.
- [34] İ. Kaya, A. Aydın, Chin. J. Polym. Sci. 27 (2009) 465.
- [35] A. Aydın, İ. Kaya, Org. Electron. 14 (2013) 730.
- [36] I. Kaya, A. Aydın, J. Appl. Polym. Sci. 121 (2011) 3028.
- [37] İ. Kaya, A. Aydın, e-Polymers 071 (2008) 1.
- [38] Y. Li, J. Ding, M. Day, Y. Tao, J. Lu, M. D'iorio, Chem. Mater. 16 (2004) 2165.
- [39] İ. Kaya, M. Yıldırım, A. Aydın, Org. Electron. 12 (2011) 210.
 [40] S.A.P. Guarìn, W.G. Skene, Mater. Lett. 61 (2007) 5102.

- [41] T. Darmanin, F. Guittard, Langmuir 25 (2009) 5463.
- [42] D. Qiu, Y. Guo, H. Wang, X. Bao, Y. Feng, Q. Huang, J. Zeng, G. Qiu, Inorg. Chem. Commun. 14 (2011) 1520.
- [43] R. Pernites, R. Ponnapati, M.J. Felipe, R. Advincula, Biosens. Bioelectron. 26 (2011) 2766.
 [44] N. Behrer, F. Febrer, Francisco, D. Bewert, F. Chandrana, G. Gulli, J. Phys. Chan. 7
- [44] N. Berton, I. Fabre-Francke, D. Bourrat, F. Chandezon, S. Sadki, J. Phys. Chem. B 113 (2009) 14087.
- [45] S. Beyazyıldırım, P. Çamurlu, D. Yılmaz, M. Güllü, L. Toppare, J. Electroanal. Chem. 587 (2006) 235.
 [46] H.C. Söyleyici, M. Ak, Y. Şahin, D.O. Demikol, S. Timur, Mater. Chem. Phys. 142
- (2013) 303. [47] S.D.D.V. Rughooputh, M. Nowak, S. Hotta, A.J. Heeger, F. Wudl,
- Macromolecules 20 (1987) 212.
- [48] E. Yildız, P. Çamurlu, C. Tanyeli, I. Akhmedov, L. Toppare, J. Electroanal. Chem. 612 (2008) 247.